λ = dimensionless axial position
ω = frequency, rad./hr.
θ = time, hr.

Subscripts

g = gas phase
in = gas phase inlet
j = radial mesh point location
k = axial mesh point location
l = liquid phase

Coefficients in Gas Phase Equations (17), (18), (19), and (23)

$$A_0 = -\frac{1}{n} - \frac{2D}{m^2}$$

$$B_0 = \frac{2D}{m^2}$$

$$F_0 = \frac{2D}{m^2} - \frac{1}{n}$$

$$A_j = \frac{1-\rho_j^2}{n} - \frac{D}{m^2} \quad 1 \leqq j_g \leqq N_g - 1$$

$$B_j = \frac{D}{2m^2} + \frac{D}{4\rho_j m} \quad 1 \leqq j_g \leqq N_g - 1$$

$$C_j = \frac{D}{2m^2} - \frac{D}{4\rho_j m_2} \quad 1 \leqq j_g \leqq N_g - 1$$

$$E_j = \frac{D}{m^2} - \frac{1-\rho_j}{n} \quad 1 \leqq j_g \leqq N_g - 1$$

Coefficients in Liquid Phase Equations (20), (21), (22), and (24)

$$A_j = -\frac{1-\rho_j^2}{n} - \frac{D}{m^2} \quad 1 \leqq j_l \leqq N_l - 1$$

$$B_j = \frac{D}{2m^2} + \frac{D}{4[(R_g/R_l) + \rho_j]m} \quad 1 \leqq j_l \leqq N_l - 1$$

$$C_j = \frac{D}{2m^2} - \frac{D}{4[(R_g/R_l) + \rho_j]m} \quad 1 \leqq j_l \leqq N_l - 1$$

$$E_j = \frac{D}{m^2} - \frac{1-\rho_j^2}{n} \quad 1 \leqq j_l \leqq N_l - 1$$

$$A_N = -\frac{D}{m^2}$$

$$C_N = \frac{D}{m^2}$$

$$E_N = \frac{D}{m^2} - \frac{1-\rho_j^2}{n}$$

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Mass Transfer Limitations in a Trickle-Bed Reactor

CHARLES N. SATTERFIELD, A. A. PELOSSOF,
and THOMAS K. SHERWOOD

Massachusetts Institute of Technology, Cambridge, Massachusetts

The hydrogenation of alpha-methylstyrene to cumene at 20 to 50°C. was studied experimentally with a trickle-bed reactor comprising a single vertical column of spherical porous palladium-on-alumina catalyst pellets. Other studies with powdered catalyst and studies in which catalyst pellets were swirled in a reactor allowed the intrinsic kinetics and effectiveness factor of the catalyst pellets to be determined. At 50°C. the reaction rate in the trickle-bed was about one-half of that in the absence of mass transfer limitations in the outside liquid film. The effectiveness factor of the pellets alone at 50°C. was 0.0057, and the tortuosity factor was 7.5. Experimental results are compared with four theoretical models for trickle-bed reactors and criteria are presented for estimating whether mass transfer through the outside film is a significant resistance in an industrial trickle-bed reactor.

A trickle-bed reactor consists of a fixed catalyst bed in which the liquid reactant flows over the catalyst pellets while the reacting gas, which fills the voids, flows either in the same or opposite direction. The rate-controlling step can be one or a combination of the following processes: (a) mass transfer of reactants and/or products between the bulk gas phase and the liquid-gas interface, (b) mass transfer through the liquid film surrounding the pellets, (c) diffusion and simultaneous reaction within the liquid-filled catalyst pores, and (d) intrinsic kinetics of reaction at the catalyst surface. The object of this study was to determine the role played in the performance of a trickle-bed by the resistance to mass transfer of the reacting gas through the liquid film. The reactant concentration at the boundary between catalyst outside surface and liquid film is affected by the simultaneous diffusion and reaction within the catalyst pellets so such a study must also include that of the effectiveness factor of the catalyst as such.

The trickle-bed reactor has been developed by the petroleum industry primarily for hydrodesulfurization, hydrocracking, and the hydrotreating of various petroleum fractions of relatively high boiling point (*6*, *12*). Under reaction conditions, the feed is frequently a vapor-liquid mixture which is reacted at liquid hourly space velocities [LHSV in volume of fresh feed, as liquid/(volume of bed)(hr.)] in the range of 0.5 to 4, in the case of hydrodesulfurization. Both direct costs and capital costs are claimed to be 15 to 20% less for the trickle-bed operation than for the equivalent hydrodesulfurization unit operating entirely in the vapor phase (*6*). Furthermore, it is desired to treat many stocks of such high boiling point that vapor-phase operation is impossible without excessive cracking. One can foresee the extension of application of trickle-bed reactors to other catalytic gas-liquid reactions as more becomes known about their design and operating characteristics. Unlike the slurry reactor, a trickle-bed reactor approaches plug flow behavior and the problem of separating the catalyst from the product stream does not exist. The low ratio of liquid to catalyst in the reactor minimizes the extent of homogeneous reaction.

Very little information is available regarding mass transfer limitations in trickle-beds. In some laboratory studies of trickle-bed reactors the rate of reaction appeared to be limited by intrinsic reaction kinetics rather than a mass transfer process (*1*, *13*). Le Nobel and Choufoer in a study of the performance of a laboratory trickle-bed reactor representative of the Shell hydrodesulfurization process (*8*), found that reduction in catalyst size increased the reaction rate, indicating pore diffusion limitations. Reduction in the feed liquid viscosity by addition of a diluent also increased the reaction rate; this was attributed to an increase in diffusivity of organosulfur molecules through the liquid-filled pores. These results were discussed further by van Deemter (*23*). The oxidation of ethanol to acetic acid over a palladium-bearing catalyst in a trickle-bed reactor was studied by Klassen and Kirk (*7*), but because of the numerous parameters involved, it was difficult to determine the exact contribution of each possible resistance.

The rate of reaction in a trickle-bed reactor also depends on the extent of liquid maldistribution (*15*), that is, the nonuniformity of liquid flow over the catalyst pellets. A disproportionate amount of liquid will frequently flow near the wall where the void fraction is greatest, depending largely on the ratio of the diameter of the column to that of packing. There is disagreement concerning the critical value of this ratio above which maldistribution becomes insignificant (*2*, *18*, *19*), but above a ratio of about 25 to 1, which is usually greatly exceeded in commercial reactors, it is probably unimportant. In industrial trickle-bed reactors the problem of maldistribution is largely that of initial distribution of liquid, so the reactor must be equipped with distributors which will provide a uniform liquid feed onto the top layer of catalyst pellets.

THEORY

The present experimental study employed a single vertical column of spherical pellets. This arrangement was chosen to avoid the problems of maldistribution and to provide uniform flow of liquid over the catalyst pellets. The dynamic holdup and mass transfer characteristics of the liquid on the pellets in the reactor can be estimated by making the following assumptions: (a) flow in the liquid film around the spherical pellet is laminar with a parabolic velocity profile, (b) streamlines are parallel to the catalyst surface, that is, the liquid has no velocity component perpendicular to the surface, (c) the gas exerts no drag on the liquid, (d) when liquid is flowing downwards there is no significant addition to the liquid held in the lenses between adjacent spheres, which comprises the static holdup, and (e) mass transfer in the direction perpendicular to the flow is by diffusion only.

Holdup

Consider a liquid film falling around a solid sphere and focus attention on the element *ABCD* shown in Figure 1. This is a section of an annular shell in three dimensions of thickness dx, radius $R + (\Delta - x)$, and height $d\theta$. By a material balance the relation between the volumetric flow rate, L, the surface velocity, U_i, the pellet radius, R, and the film thickness at angle θ to the vertical is found to be (*14*):

$$L = \frac{4}{3}\pi U_i R \Delta \sin\theta \tag{1}$$

By a force balance on the same element *ABCD*,

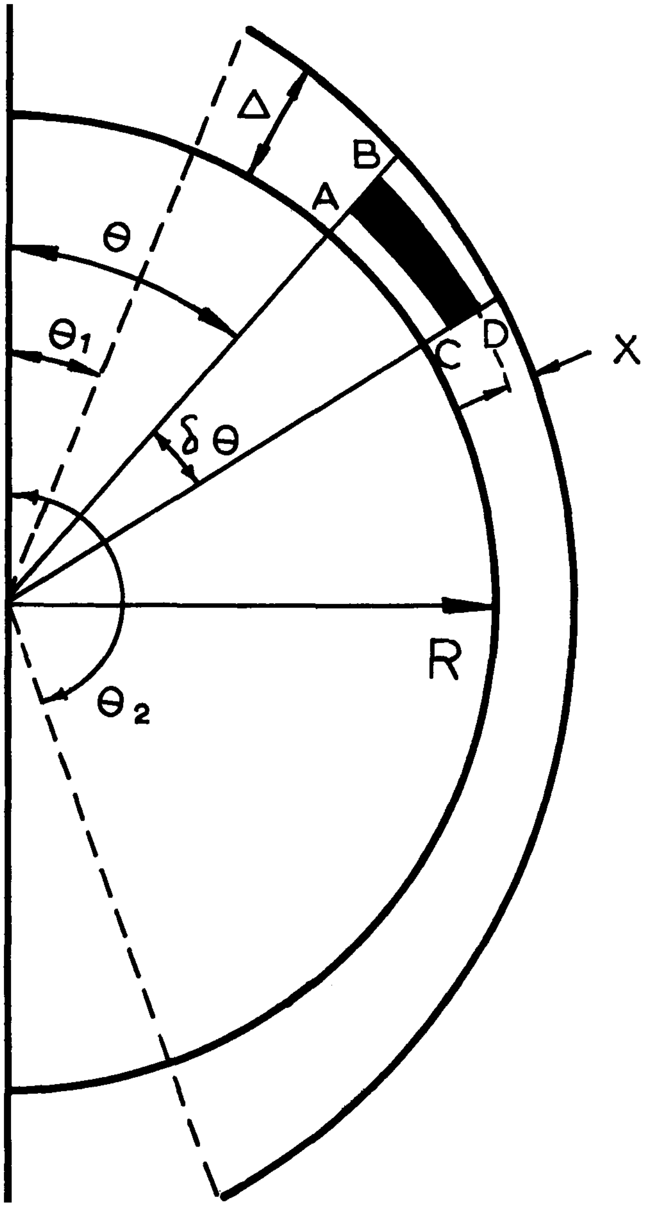


Fig. 1. Analytical model.

$$U_i = \frac{\rho g \Delta^2}{2\mu} \sin\theta \qquad (2)$$

where μ and ρ are the viscosity and density of the liquid, and g is the acceleration due to gravity. Eliminating U_i from Equations (1) and (2)

$$\Delta = \left(\frac{3L\mu}{\pi d \rho g} \right)^{1/3} \sin^{-2/3}\theta \qquad (3)$$

where d is the particle diameter, $2R$. The total holdup on a packed bed is composed of two terms, the static holdup caused by surface tension forces at the lenses at the points of contact of the pellet, and the dynamic holdup caused by the flowing liquid;

$$h_T = h_D + h_S$$

and

$$h_D = \rho \int_{\theta_2}^{\theta_1} \Delta \cdot dA \qquad (4)$$

As part of assumption number (*4*) above, the liquid is considered as moving between θ_1 and θ_2. Substituting Equation (3) into Equation (4) for N spheres,

$$h_D = N\left(\frac{3\mu L}{d\pi\rho g} \right)^{1/3} \left(\frac{\rho\pi d^2}{2} \right) \int_{\theta_1}^{\theta_2} \sin^{1/3}\theta \cdot d\theta \qquad (5)$$

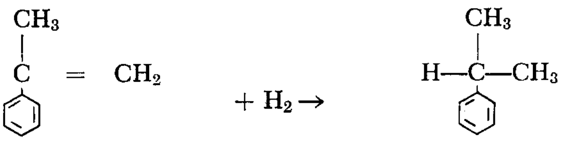
Turner and Hewitt (*22*) reported measurements of static holdup for a variety of liquids, and correlated their data by an equation based on dimensionless analysis:

$$\left(\frac{m}{\rho d^3} \right) = 0.41 \left(\frac{\gamma}{\rho d^2 g} \right)^{0.79} \qquad (6)$$

where m is the weight of the liquid in the lens between two spheres, and γ is the surface tension. Malcor (*11*) has developed the theory of the liquid contained in a single lens with allowance for the effect of gravity in distorting the curvature of the liquid surface.

Mass Transfer Through Liquid Film

The model reaction chosen for study was the hydrogenation of liquid alpha-methylstyrene to form cumene on a 1% palladium-on-alumina catalyst.



Cumene is the only reaction product and essentially no homogeneous reaction ocurs (*1*). A rapid reaction rate can be obtained at temperatures only slightly above ambient, at which the vapor pressures of alpha-methylstyrene and cumene are quite low, so that the reaction product remains in the liquid phase. Resistance to transport of hydrogen through the gas phase is negligible when pure hydrogen is used. The intrinsic chemical kinetics were well characterized in an associated study (*10*, *16*). The reaction is first-order with respect to hydrogen (*16*). The feed was pure alpha-methylstyrene and overall conversions were much less than 1%.

The molar mass flux is the product of the diffusivity and the concentration gradient and by stoichiometry must be equal for alpha-methylstyrene and hydrogen under steady state conditions. Since the alpha-methylstyrene is present at much higher concentrations than hydrogen, the rate of diffusion of hydrogen in the liquid becomes rate-limiting before that of alpha-methylstyrene. For laminar film flow over a spherical pellet, mass transfer is a combination of two processes: a diffusional process which predominates in the direction normal to flow and a convective process which predominates in the direction of flow. By a mass balance on hydrogen in element *ABCD* in Figure 1 and neglecting $(\Delta - x)$ relative to R in the final form of the equation, one obtains for steady state conditions (*14*):

$$DR^2 \left(\frac{\partial^2 c}{\partial x^2} \right) - 2D \left(\frac{\partial c}{\partial x} \right) - U \left(\frac{\partial c}{\partial x} \right) = 0 \qquad (7)$$

where x is the radial distance between the outer liquid film surface and the point of interest, D is the molecular diffusivity of hydrogen in the liquid, and c is the hydrogen concentration.

The boundary conditions are:

$$\begin{array}{lll} \theta = \theta_1 & \Delta \geqq x \geqq 0 & c = c^* \\ x = 0 & \theta_2 \geqq \theta \geqq \theta_1 & c = c^* \\ x = \Delta & \theta_2 \geqq \theta \geqq \theta_1 & \end{array}$$

$$D\left(-\frac{\partial c}{\partial r} \right) = \frac{\phi_s c_s D_{\text{eff}}}{R} \left[\frac{1}{\tanh\phi_s} - \frac{1}{\phi_s} \right]$$

where c_s is the hydrogen concentration in the liquid at the pellet surface, D_{eff} is the effective diffusivity in the liquid-filled porous pellet, and ϕ_s is the Thiele modulus.

The first boundary condition specifies that the liquid at the top of the pellet is saturated with hydrogen, but this is applicable to the first pellet only. The entry concentration for each subsequent pellet will depend on the extent of liquid mixing which occurs at the junction between adjacent pellets. Two extreme limiting conditions were considered in the mathematical model, complete mixing between pellets, or no mixing at all. Equation (7) was solved by computer calculations using a finite difference technique, applying one or the other of these two limiting assumptions. The computer programs are given by Pelossof (*14*). In the mixed model the entry concentration to the pellet was taken to be the flow-averaged value of the exit concentration for the pellet above it. In the nonmixed model the concentration profile at entry is identical to that leaving the pellet above, that is, this model is analogous to that for a theoretical wetted wall column. The concentration at the outer surface of the catalyst pellet, c_s, varies slightly with position and is set by equating the mass flux to the pellet surface to that into the interior of the pellet.

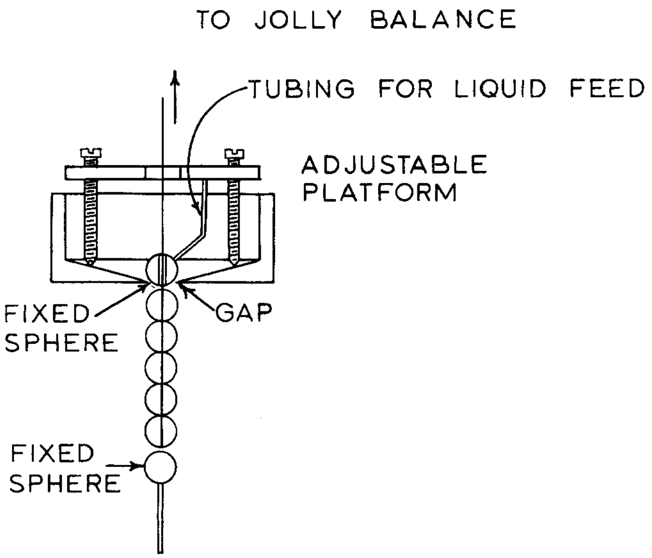


Fig. 2. Holdup apparatus, detail.

EXPERIMENTAL PROCEDURE

The experimental program was divided into three parts: (a) determination of dynamic and static holdup for a liquid on a vertical column of spheres as a function of the physical properties of the liquid and its flow rate; (b) an investigation of the rate of hydrogenation of alpha-methylstyrene on a simulated trickle-bed reactor consisting of a vertical column of catalyst spheres; (c) estimation of the intrinsic reaction rate by studies with powdered catalyst in a well-stirred reactor and of the rate in the absence of outside film limitations by studies on catalyst pellets swirled at high speed in a reactor.

Holdup

Liquid holdup was measured by weighing a column of five etched glass spheres over which liquid was allowed to run, by means of a precalibrated spring. In order to minimize liquid entry and exit effects, the column of five spheres (each 3/8 in. in diameter) was suspended between two other fixed spheres. The top fixed sphere contained a centrally drilled 1/16 in. hole which allowed vertical movement of the wire supporting the lower column (see Figure 2).

The liquid, butanol, methanol, or water, was pumped from a reservoir into a constant head tank and from there fed onto the top fixed sphere. The size of an annular gap surrounding this sphere (Figure 2) could be varied by adjusting three screws on the platform supporting the top fixed sphere, thus obtaining uniform flow around the spheres. Weight measurements were recorded for totally dry spheres, for static holdup on spheres, and for flow rates ranging between 0 and 150 cc./min.

Trickle-Bed Reactor

The reaction was carried out in a cylindrical glass reactor containing a vertical column of fourteen catalyst pellets supported as shown in Figure 3. The catalyst contained 1% wt. palladium impregnated on a spherical porous alumina support. Although the method of preparation was aimed at producing as nearly uniform concentration as practicable, it was subsequently found that the palladium distribution within the pellets was less uniform than desired. Electron microprobe analyses (M.I.T., Metallurgy dept.) were performed on two of the pellets after they were cut in half, and in two directions across each pellet. The palladium concentration profile as a function of radial distance was essentially the same in each case, a typical profile being shown in Figure 4. The concentration was essentially uniform over the first 100μ and then dropped steadily, rising again to its outside concentration over a band about 1,750 to 2,000μ in from the outside surface and then decreasing rapidly to zero. This implies that the catalyst support consisted of a 100μ thick fine shell surrounding a coarser section and then a second fine-pore inner shell. The intensity of blackness to the eye corresponded to this profile; the centers of the spheres were white. This palladium concentration distribution did not affect the present results because, as will be shown, the reaction all occurred within the outer 100μ layer.

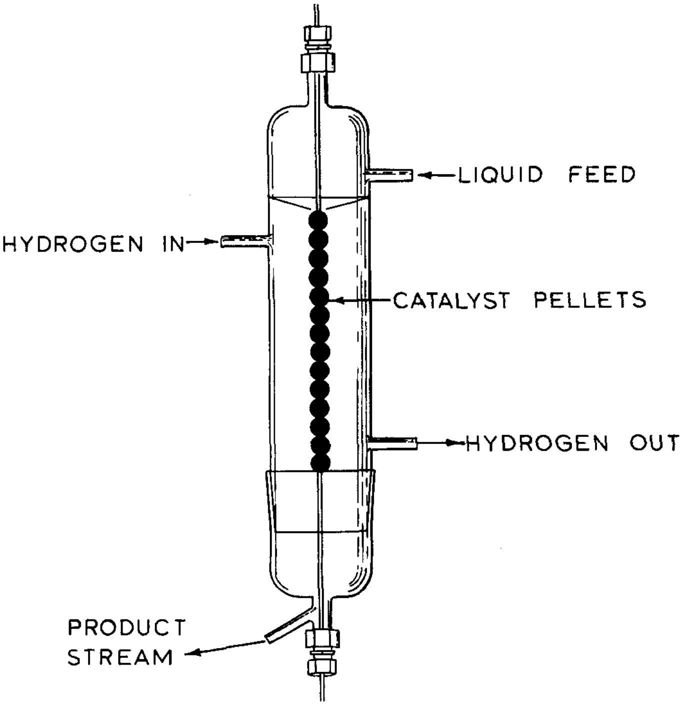


Fig. 3. Trickle-bed reactor.

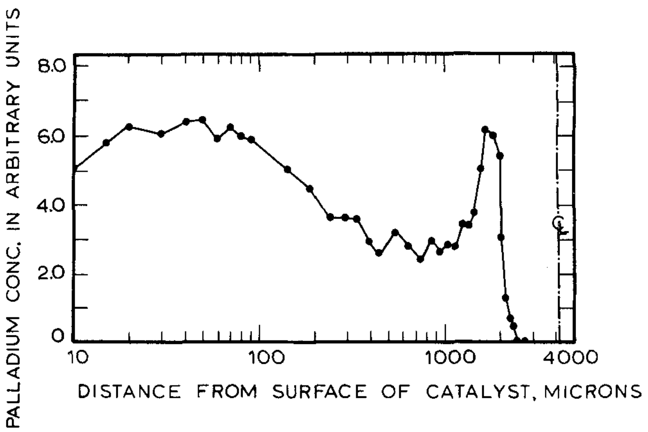


Fig. 4. Electron microprobe analysis of catalyst.

The diameter of the pellets was 0.825 cm., their bulk density 1.62 g./cc., and their void fraction 0.498. A mercury porosimeter measurement revealed that 83% of the void volume was occupied by pores between 120Å. and 180Å. in diameter, 10% by pores smaller than 120Å., and the rest by pores larger than 180Å. in diameter.

Hydrogen was purified to remove trace amounts of oxygen by passage through a bed of palladium on asbestos, and the resulting water was removed in a bed of silica gel. The hydrogen was then admitted into the top of the reactor, proceeded downwards and was eventually vented to the atmosphere through an oil trap. The entire system was maintained at all times under a small positive pressure (1 to 2 cm. water above atmospheric), so that in the case of leaks no back flow of air onto the catalyst would occur.

Pure liquid alpha-methylstyrene was pumped into the reactor by a variable speed stainless steel Zenith gear pump. The liquid was fed onto the pellets through a small funnel located at the top of the reactor. The product stream was then passed through a three-way stopcock into a reservoir. Samples could be withdrawn from the third outlet of the stopcock.

The reaction studies covered a flow range from 0.1 to 0.7 cc./sec. at 22, 31, 40, and 50°C. and 1 atm. hydrogen pressure. In all these runs the alpha-methylstyrene was presaturated with hydrogen. Two runs were performed with 40 and 70% vol. hydrogen in nitrogen, and with the alpha-methylstyrene saturated with the same mixture of gases. The amount of cumene in the product streams was determined by the use of a dual flame ionization chromatographic unit. The feed reservoir and reactor were both placed in a single large constant-temperature enclosure.

Studies in a Stirred Reactor

The characteristics of the reaction on the catalyst in the absence of mass transfer effects were determined in a reactor constructed by Ma and described elsewhere (*10, 16*). It consisted essentially of a 3-liter baffled kettle containing a centrally located shaft equipped with four paddlelike baskets on its lower end into which catalyst pellets could be placed, or which could be used to achieve good suspension of a powdered catalyst.

Reaction rate measurements were made at 50°C. with 0.11 g. of finely powdered (diameter < 40μ) palladium-rich sections of the catalyst (corresponding to the black parts of a pellet used in the trickle-bed study) together with 1,816 g. of alpha-methylstyrene. Liquid samples were taken every 15 min. for 75 min. at 800 rev./min. after which the speed was stepped up to 1,000 rev./min., and again samples were withdrawn every 15 min. for 60 min. The extent of the conversion to cumene was determined by gas chromatography. The procedure with whole pellets was similar except that six

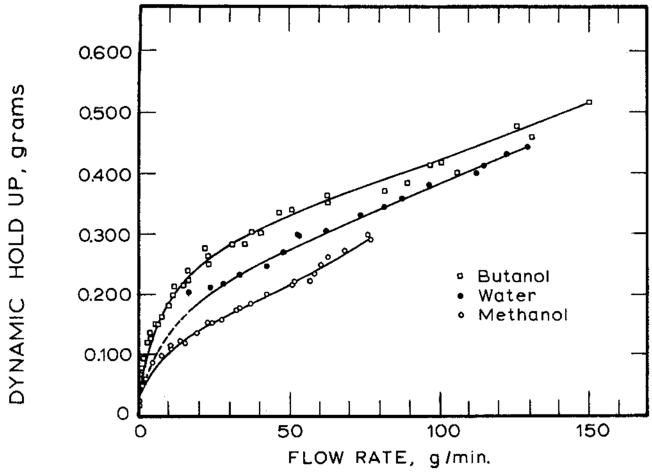


Fig. 5. Experimental dynamic holdup: five ⅜ in. spheres.

of the original catalyst pellets were inserted into the baskets, the shaft speed was maintained throughout at 800 rev./min., and samples were withdrawn every 30 min. for 3 hr.

DISCUSSION OF RESULTS

Holdup

Figure 5 shows the experimental dynamic holdup data for methanol, water, and butanol as determined by subtracting the static holdup from the total holdup. The results for water below about 30 g./min. became increasingly meaningless because of incomplete wetting of the spheres. Experimental error amounted to ± 0.5 and ± 10% at high and low flow rates, respectively.

The integral of Equation (5) was determined by substituting the values of θ_1 and θ_2 obtained from photographs of the static holdup for butanol. These were 33 and 147 deg., respectively, and were assumed to be the same for methanol and water. (The values for alpha-methylstyrene on the slightly smaller reactor pellets were 35 and 145 deg.) The resulting equation is:

$$h_D = 1.875\,N \left(\frac{3\mu L}{d\pi\rho g}\right)^{1/3} \left(\frac{\rho\pi d^2}{2}\right) \qquad (8)$$

An error of ± 5% in the value of θ is equivalent to about ± 4% variation in the integral of Equation (5). Equation (8) may be reduced to the following dimensionless form:

$$\frac{h_D}{\rho d^3} = 1.98\,N \left(\frac{L\rho\pi}{\mu d}\right)^{1/3} \left(\frac{\rho^2 g d^3}{\mu^2}\right)^{1/3} \qquad (9)$$

where $(L\rho\pi/\mu d)$ is the Reynolds number for the system considered.

Figure 6 is a graphical presentation of the data with the ordinate and abscissa corresponding to the left-hand side of Equation (9) and N_{Re}, respectively. In the region of N_{Re} of 10 to 600, the experimental results are within ± 10% of the theoretical model represented by line *AB*. For $N_{Re} < 10$ the results fall below the theoretical line, which is probably due to magnified experimental error and poor wetting. For $N_{Re} > 600$ the data fall consistently above line *AB* which may be ascribed to the inertia effects on the flow pattern which were not considered in the development of Equation (8). A similar observation was made by Davidson and co-workers (*4*) for water falling over a vertical row of table tennis balls. It may be concluded that for N_{Re} between 10 and 600 the film thickness over a pellet, for the systems considered here, is well represented by Equation (3).

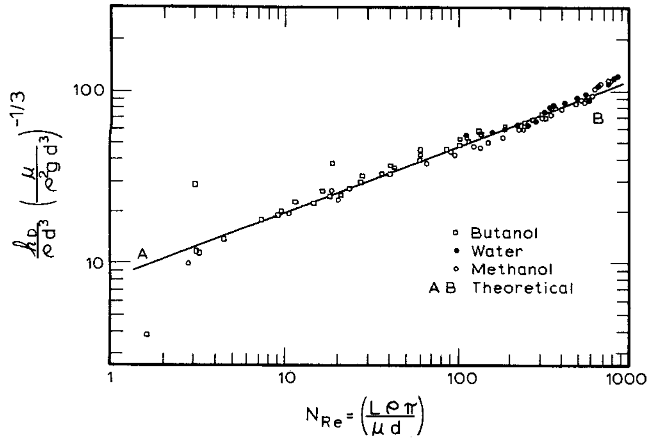


Fig. 6. Correlated dynamic holdup for five spheres.

An average film thickness may be defined by averaging Δ from Equation (3) over the flow region, from 33 to 147°. The resulting equation is:

$$\bar{\Delta} = 0.112 \left(\frac{L\mu}{d_p}\right)^{1/3} \qquad (10)$$

For the reaction system, $\bar{\Delta}$ = 0.0118 cm. at 50°C. and at the lowest flow rate studied, which was 0.133 cc./sec. (1.01 × 10^{-3} g.moles/sec.). The highest flow rates in the reaction system correspond to an average film thickness of about 0.02 cm. The liquid film around catalyst pellets in the Shell hydrodesulfurization process has been reported to average between 0.001 and 0.01 cm., depending on flow conditions (*23*).

The static holdup data for a single lens are compared in Table 1 with those predicted by the correlation derived by Turner and Hewitt (*22*). The predicted values are about 50% of those measured, which may result from the fact that the correlation was established from holdup data on smooth spheres whereas those used in the present study were etched.

TABLE 1. COMPARISON BETWEEN EXPERIMENTAL AND PREDICTED STATIC HOLDUP

	Water	Butanol	Methanol
Experimental, g.	0.080	0.043	0.038
Predicted, g.	0.049	0.020	0.019

Trickle-Bed Reactor

The observed rates of reaction as a function of liquid flow rate and reaction temperature are summarized in Figure 7. In all the runs presented the alpha-methylstyrene was presaturated with hydrogen. The open and dark points

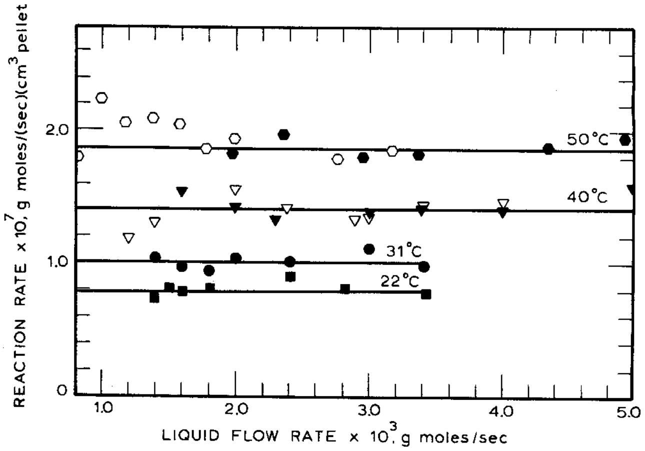


Fig. 7. Reaction rates for trickle-bed reactor, hydrogen pressure, 1 atm.

at 50 and 40°C. correspond to two separate series of runs, the second series being several days later than the first to ascertain reproducibility. All the runs were made on one set of catalyst spheres.

Conversions in the reactor varied between 0.92×10^{-2} and 9.25×10^{-2} mole % cumene for the high flow rates at 22°C. and low flows at 50°C., respectively. The experimental error associated with these values was ± 20% and ± 5%. These conversions are so low that the reactor may be regarded as isothermal. Even under adiabatic conditions, 1% conversion would cause only about a 5°C. temperature rise. Complete reaction of the hydrogen originally dissolved in the alpha-methylstyrene would correspond to a conversion of 4.7×10^{-2} mole % cumene at 50°C., or 3.7×10^{-2} mole % cumene at 22°C. The minimum conversion observed at 22°C. was thus equivalent to the consumption of only about 25% of the original hydrogen dissolved in the liquid and the maximum conversion at 50°C. to about double the amount of the original hydrogen.

From Figure 7 it appears that liquid flow rate had no significant effect on the reaction rate within the magnitude of the experimental error. The higher reaction rates at low flow rates at 50°C. are believed to be due to premature sample collection. Since the catalyst was exposed to a stream of hydrogen prior to start-up, both the catalyst pores and the palladium were initially saturated with hydrogen. As a result, the initial reaction rate was greater than at steady state. This equilibration period lasted for about 2½ hr. at a liquid flow of 0.246 cc./sec.

The results obtained with hydrogen-nitrogen mixtures at 50°C. and 1 atm. total pressure at a liquid flow of 0.246 cc./sec. and gas flow of 1.56 cc./sec. are shown in Figure 8. Estimates of the correction to account for the gas-phase mass transfer resistance are indicated on the graph. Within experimental error the observed reaction in the trickle-bed is first-order with respect to hydrogen. However, a first-order process would be observed in the presence of significant pore diffusion limitations (*17*), mass transfer limitation in the liquid film, or even if the intrinsic kinetics were rate-limiting (*16*).

Activation Energy

Figure 9 is an Arrhenius plot of the observed reaction rate constant. The apparent activation energy as determined from the slope is 5,080 ± 500 cal./g. mole. The activation energy for the intrinsic kinetics of the reaction on an 0.5% palladium/alumina catalyst was determined experimentally by Ma to be 7,600 cal./g. mole. Both catalysts were prepared by impregnating a support with a palladium salt which was subsequently reduced, so that it is reasonable to assume the intrinsic activation energy is about the same for both catalysts.

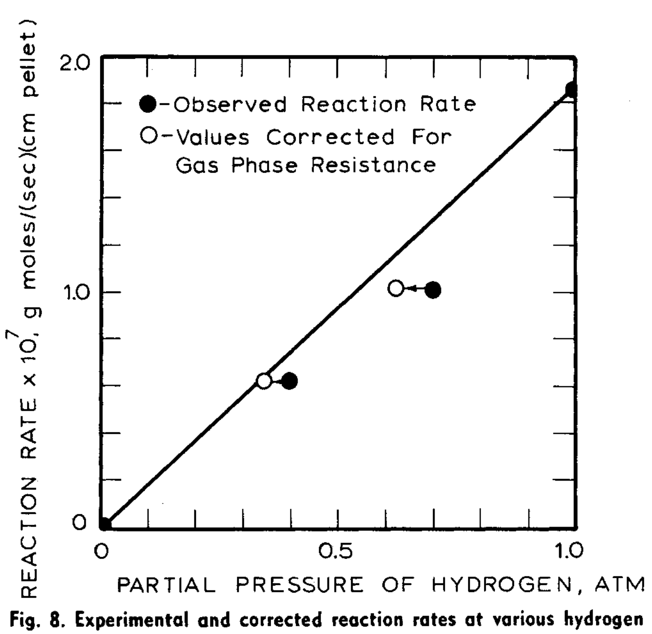


Fig. 8. Experimental and corrected reaction rates at various hydrogen partial pressures, 50°C. and 1 atm. total pressure.

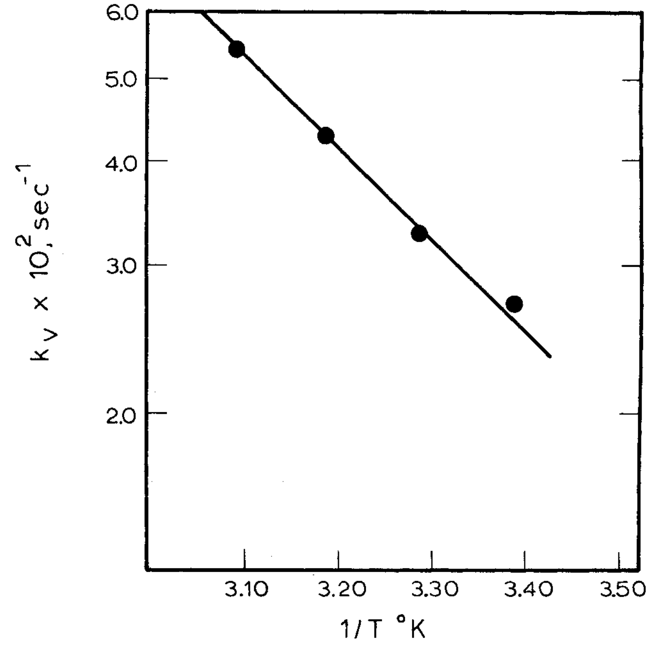


Fig. 9. Arrhenius graph of first-order rate constant in trickle-bed reactor.

If pore diffusion is a significant limitation the observed rate constant is proportional to $\sqrt{D_{\text{eff}} k_v}$ and the apparent activation energy, $E_{\text{app}} = (E_D + E)/2$. The activation energy for bulk diffusion of hydrogen in alpha-methylstyrene or cumene as determined by Ma (*16*) is about 3,000 cal./g. mole. Therefore the predicted value for E_{app} is $(7,600 + 3,000)/2 = 5,300$ cal./g. mole. This is closely comparable to the observed activation energy in the trickle-bed reactor and indicates the existence of substantial pore diffusion limitations.

In the presence of mass transfer limitations within both the liquid film and the catalyst pores the experimentally observed activation energy should have a value between that for a reaction limited by pore diffusion and that for bulk diffusion, that is, between 5,300 and 3,000.

Powdered Catalyst

The reaction rate at 50°C. and 1 atm. hydrogen pressure was 5.96×10^{-5} g.moles/(sec.)(cc. pellet). An estimate of the mass transfer coefficient based on the settling velocity of the largest particles (40μ) indicated that under the experimental conditions mass transfer limitations from bulk liquid to outside catalyst surface were negligible; the hydrogen concentration at the catalyst surface was, therefore, the equilibrium value at 50°C. and 1 atm. pressure. The effectiveness factor for the largest of the crushed particles was estimated to be about 0.75. Considering that only a small fraction of the particles were as large as 40μ in diameter, the assumption that the rate measured with the powdered catalyst was the intrinsic rate is valid.

Whole Pellets in Stirred Reactor

The observed reaction rate with the whole pellets in the stirred reactor at 50°C. and 1 atm. hydrogen pressure was 3.42×10^{-7} g.moles/(sec.)(cc. pellet). This value is considerably smaller than that for the powdered catalyst, indicating the presence of significant pore diffusion limitations in the pellets. Mass transfer resistance from bulk liquid to outside surface of the catalyst pellets was estimated to be negligible on the basis of mass transfer coefficients measured by dissolving benzoic acid pellets in water in the same apparatus. Details are given elsewhere (*16*).

Assuming that the reaction rate observed with the powdered catalyst was indeed the intrinsic rate, then the effectiveness factor, η, for the original catalyst pellets at 50°C. is $3.42 \times 10^{-7}/5.9 \times 10^{-5} = 5.75 \times 10^{-3}$, and the Thiele modulus $\phi_s = 3/\eta = 521$. Only the outermost portions of the pellets could have contributed to the reaction. For a first-order reaction and ϕ_s of 521, the concentration at a point 1% in from the outside surface (depth of 25μ) is only 0.54% of that at the surface.

At 50°C. the solubility of hydrogen in alpha-methylstyrene is 3.54×10^{-6} g. mole/cc. (*16*) and the intrinsic rate constant $k_v = 16.8$ sec.$^{-1}$. The bulk diffusivity of hydrogen in alpha-methylstyrene $= 1.65 \times 10^{-4}$ sq.cm./sec. (*16*). For first-order reactions $\phi_s = R\sqrt{k_v/D_{\text{eff}}}$, where $D_{\text{eff}} = D\theta/\tau$, from which the catalyst tortuosity τ was calculated to be 7.5. The fact that τ is proportional to the square of ϕ_s somewhat reduces the accuracy with which it can be determined as well as the fact that it incorporates the errors associated with the solubility and diffusion coefficient for hydrogen. For a pelletized palladium-on-alumina catalyst Ma (*10, 16*) found a value of $\tau = 3.9$ from data on the same reaction analyzed in the same way. Cadle (*3*) measured counterdiffusion fluxes of gases at high pressure, which were essentially in the bulk mode, through five different commercial catalyst pellets. Values of τ varied from 2.8 to 7.5.

Mass Transfer through the Liquid Film in Trickle-Beds

The possibility of mass transfer limitation is greatest at the highest temperature, 50°C. By simply comparing the reaction rates at 50°C. and 1 atm. hydrogen pressure for the trickle-bed (1.86×10^{-7} g.moles/(sec.)(cc. pellet) and that in the swirling pellet reactor (3.42×10^{-7} g. moles/(sec.)(cc. pellet), it is clear that some resistance exists in the liquid film. The magnitude of this resistance may be determined by equating the flux through the liquid film to the rate of reaction, both taken per unit of outside surface area of pellet.

$$k_{Ls}(c^* - c_s) = \frac{\phi_s D_{\text{eff}} c_s}{R}\left[\frac{1}{\tanh \phi_s} - \frac{1}{\phi_s}\right] \qquad (11)$$

The rate of reaction is proportional to $\overline{c}_s$ and in the swirling pellet reactor, $\overline{c}_s = c^*$. Hence in the trickle bed reactor $\overline{c}_s = (3.54 \times 10^{-6})(1.86/3.42) = 1.93 \times 10^{-6}$. The value of k_{Ls} is then found from Equation (11) to be 1.59×10^{-2} cm./sec. For comparison, a value of k_{Ls} can be calculated assuming a simple stagnant film model, that is, $k_{Ls} = D(\overline{1/\Delta})$. At the lowest liquid flow rates studied (0.133 cc./sec.), where experimental accuracy is highest, $\overline{\Delta}$ is 0.0118 cm. and if we take $k_{Ls} = D/\overline{\Delta}$, it equals 1.4×10^{-2} sq.cm./sec., which is closely comparable. At the highest flow rate, $\overline{\Delta}$ is about 0.02 cm. and k_{Ls} by the stagnant film model would be about one-half this value. In principle, averaging should be done with respect to $1/\Delta$ rather than Δ although the difference in the final result is not great in this case. The value of $1/(\overline{1/\Delta})$ is about 12% greater than $\overline{\Delta}$.

Some feeling for the effect of a change in intrinsic activity of the catalyst on c_s can be obtained by noting that for catalyst effectiveness factors of about 0.5 or less (high values of ϕ_s) the bracketed term in Equation (11) approaches unity. For a first-order reaction, $\phi_s = R\sqrt{k_v/D_{\text{eff}}}$ which upon substitution in Equation (11) yields:

$$k_{Ls}(c^* - c_s) = c_s\sqrt{(k_v)(D_{\text{eff}})} \qquad (12)$$

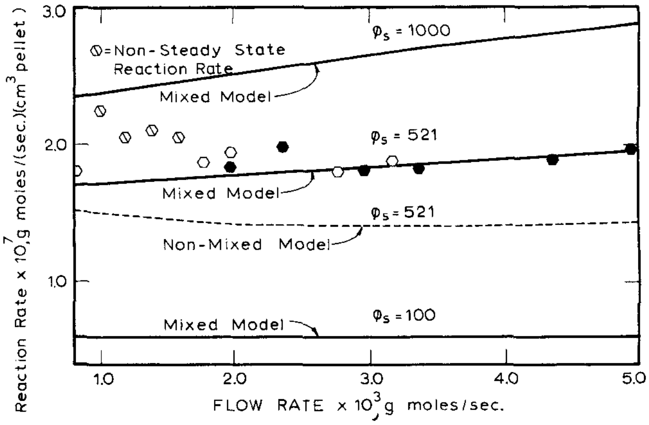


Fig. 10. Comparison of mixed and nonmixed models with experimental data at 50°C. and 1 atm. pressure. The experimental points are the same as those shown in Figure 7 for 50°C.

COMPARISON WITH MODELS

Figure 10 compares the experimental reaction rates at 50°C. in the trickle-bed reactor with those predicted by the mixed and nonmixed models obtained by computer solutions of Equation (7). The only unknown parameter in the theoretical model is the catalyst effectiveness factor which was found experimentally to correspond to a Thiele modulus of 521. The agreement between the mixed model and the experimental results is excellent.

In spite of this congruence, it should be emphasized that the model is still an approximation to the actual physical behavior of the experimental trickle-bed. Photographs taken of the flow pattern with a dye injected onto the top sphere indicated that mixing between particles was incomplete, particularly at higher flow rates. However, turbulence due to rippling probably counterbalanced this behavior. Similar observations are reported by other investigators (*4, 9*) for absorption into a liquid film falling around a column of vertical spheres.

Other Theoretical Models

If the trickle-bed is operated under conditions which minimize mass transfer, namely of no turbulence or interparticle mixing, we might imagine that the mass transfer coefficient through the film would be approximated by the simple relationship: $k_{Ls} = D(\overline{1/\Delta})$, where $\overline{1/\Delta}$ is an average conductance as given by Equation (10) and the film is assumed to be stagnant. This mass transfer coefficient is compared with that from the other two models as a function of flow rate in Figure 11. (10^{-3} g.moles/sec. is equivalent to 0.132 cc./sec.). As expected, there is reasonably good agreement between the values of k_{Ls} from the nonmixed model and that from the stagnant film theory, and both are below the values calculated for the mixed model, particularly at higher flow rates. Actually, it is more realistic to regard the catalyst contact points as regions of good mixing, so the mixed model is presumably a closer approximation to reality at substantial flow rates.

An alternative to the above three models is a form of penetration theory as applied to absorption. The resistance to diffusion in the liquid on the gas side is taken to be equivalent to the reciprocal of the absorption mass transfer coefficient k_L. The resistance on the solid side is equivalent to that for the dissolution of sparingly soluble particles in a liquid film, $1/k_s$. The overall resistance is given by:

$$\frac{1}{k_{Ls}} = \frac{1}{k_L} + \frac{1}{k_s} \qquad (13)$$

Theoretical values of k_L and k_s as a function of liquid flow rate were determined by computer solutions of Equation

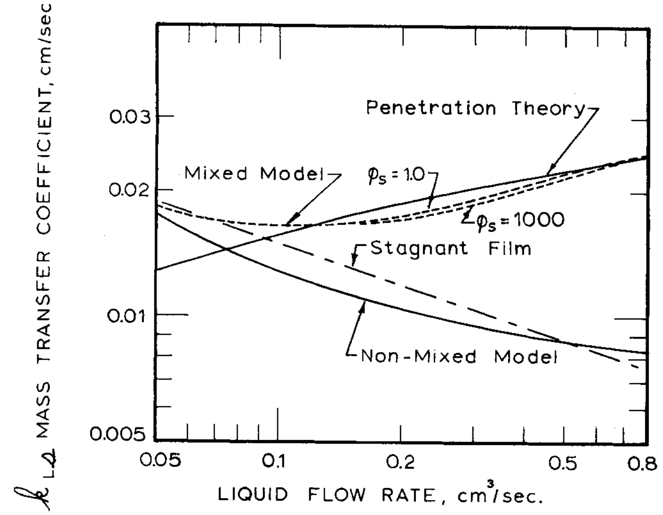


Fig. 11. Comparison of mass transfer coefficients predicted by mixed model, nonmixed model, penetration theory and stagnant film theory.

(7) for the two sets of appropriate boundary conditions, from which values of k_{Ls} were calculated from Equation (13) (*14*). These are compared in Figure 11 to those predicted from the other three models. Experimental values of k_L and k_s can also be obtained from published correlations, as illustrated in the following.

The penetration theory is only valid before the two concentration boundary layers begin to overlap, that is, at the short contact times that occur at high flow rates. At longer contact times (for example, flow rates below 0.7 cc./sec.) values of k_{Ls} predicted by Equation (13) become too high since overlap occurs and penetration theory becomes less and less representative of reality. At high flow rates the penetration theory and mixed models essentially agree with each other as they should. Slight differences between the two are caused by slightly different choices of the average value of the outside pellet surface concentration, $\bar{c}_s$. At very low flow rates, below 0.15 cc./sec., the steady state concentration profile is rapidly attained and the contribution of mixing is negligible compared to transport by diffusion across the entire film. Hence, values of k_{Ls} from the mixed and nonmixed models approach one another.

Mass transfer through the outside film cannot be a significant limitation unless the catalyst particles themselves are operating at a very low effectiveness factor. The effective diffusivity within the porous catalyst cannot normally exceed a value of about 1/5 of that in the liquid film (taking as typical values a θ of 0.5, τ of 2.5), and the thickness of the liquid film itself will always be substantially less than the catalyst radius. The interaction between catalyst effectiveness factor and flow rate may be illustrated by calculations using the mixed model (*14*). The following table gives predicted percent increases in reaction rate, g.moles/(sec.)(cc. pellet), upon increasing the liquid flow rate from 0.1 to 0.7 cc./sec., for various values of ϕ_s.

ϕ_s	η	% increase in rate of reaction
10	0.27	0.2
100	0.03	4.6
521	0.0057	15.5
1,000	0.003	39.0

It is particularly interesting to note from Figures 10 and 11 and the numbers above that flow rate is predicted to have a relatively minor effect on rate of reaction per unit volume of catalyst even though substantial mass transfer through the film exists, as would occur with high values of ϕ_s.

Industrial Trickle-Beds

The preceding discussion leads to a method of determining, in an industrial trickle-bed reactor, if mass transfer through the film may be a significant resistance. Assuming that no mass transfer resistance exists within the gas phase, then by a mass balance on hydrogen diffusing through the liquid film around a single cylindrical pellet (diameter = d and length = d):

$$\left(-\frac{1}{V_c}\cdot\frac{dn}{dt}\right)\frac{\pi d^3}{4} = k_{Ls}\left(\frac{\pi d^2}{2}+\pi d^2\right)(c^*-c_s) \tag{14}$$

Simplifying,

$$\frac{d}{6k_{Ls}c^*}\left(-\frac{1}{V_c}\cdot\frac{dn}{dt}\right) = 1-\frac{c_s}{c^*} \tag{15}$$

A criterion for significant mass transfer limitations through the liquid film can be said to correspond to $c_s < 0.95\ c^*$. Applying this criterion to Equation (15) leads to the conclusion that mass transfer from the gas phase to the outer surface of the catalyst pellets will not be significant unless the inequality of Equation (16) holds.

$$\frac{10d}{3c^*}\left(-\frac{1}{V_c}\frac{dn}{dt}\right) > k_{Ls} \tag{16}$$

A conservative estimate of k_{Ls} when no information is available on either k_{Ls} or $\bar{\Delta}$ is obtained by taking it to be $2Da/\epsilon$. The maximum mass transfer resistance is $\bar{\Delta}/D$. The average film thickness may be approximated as $\bar{\Delta} = \epsilon/2a$ by assuming that 50% of the voids in the trickle-bed reactor is filled with a liquid (*15*) where a is the outside area of catalyst particles per unit volume of reactor. For example, for ⅛ in. diameter pellets, this gives a film thickness of about 1/3 mm.

The average film thickness, $\bar{\Delta}$, can be estimated from correlations for dynamic holdup in packed beds such as that of Shulman and co-workers (*21*), although these must be used cautiously since data are available primarily on packing such as Raschig rings and Berl saddles rather than typical catalyst particles and under conditions more characteristic of absorption towers than of trickle-bed reactors.

A value of k_{Ls} may also be calculated by applying the penetration theory outlined above and using correlations of experimental values of k_L and k_s in Equation (13), for example, that of van Krevelen and Krekels (*24*) for k_s and that of Sherwood and Holloway (*20*) for k_L. However, absorption mass transfer coefficients have usually been obtained for packings which are different in size and shape than those commonly used in catalytic reactors and under substantially different operating conditions so they cannot be reliably used for the present purpose.

The use of Equation (16) may be illustrated with a set of data on the Shell trickle-bed hydrodesulfurization process (*8*). At 367°C., 827 lb./sq.in.abs. pressure, and space velocity of 2.0 kg./(liter of bed)(hr.) on ⅛ in. pellets, the reaction rate $(-1/V_c)(dn/dt)$ was 1.04×10^{-6} g.moles hydrogen/(sec.)(cc. pellet). The value of ϵ is 0.36; a is 9.87. We estimate the equilibrium hydrogen concentration in the feed stock as 4.48×10^{-4} g.moles/cc., the bulk diffusivity as 5.5×10^{-4} sq.cm./sec. The left-hand side of Equation (16) becomes 2.46×10^{-3} cm./sec. A value of k_{Ls} may be calculated applying the penetration theory outlined and correlations (*20, 24*) for k_L and k_s. This gives $k_{Ls} = 1.55 \times 10^{-2}$ cm./sec. and liquid film resistance is concluded to be negligible. k_{Ls} estimated as $2Da/\epsilon$ is about 3×10^{-2} cm./sec., and the conclusion is the same.

The reaction studied here is much more rapid. At 50°C.

and 1 atm. hydrogen pressure, the left-hand side of Equation (16) is 0.145 cm./sec. which is substantially greater than the value of k_{Ls} of 1.35×10^{-2} cm./sec. predicted from stagnant film theory at the lowest flow rate studied. For the present investigation $k_v = 16.8$ sec.$^{-1}$ whereas the pseudo first-order rate constant k_v for trickle-bed hydrodesulfurization is about 2.3×10^{-3} sec.$^{-1}$. The diffusional resistance of the liquid film cannot be expected to be of importance in trickle-bed reactors operating at the volumetric reaction rates of typical commercial hydrotreating operations.

The above analysis has focused on the transfer of hydrogen as the limiting process. In many petroleum operations the goal may be a high percentage of reaction of a component present in the liquid in small concentrations, for example, an organosulfur or organonitrogen compound, in which case the transfer of such a component initially present in the liquid may be the rate-limiting process. It is evident that under these conditions the degree of mixing at the exit of each catalyst particle will have a much more profound effect on performance.

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NOTATION

A = superficial (outside) surface area of catalyst pellet per unit of catalyst pellet volume, sq.cm./cc.; $= 6/d$ for a sphere
a = superficial (outside) surface area of catalyst per unit volume of reactor, sq.cm./cc.
c = concentration, g.moles/cc.
c^* = equilibrium concentration of hydrogen in alpha-methylstyrene, g.moles/cc.
c_s = concentration of hydrogen in liquid at outside particle surface, g.moles/cc.
$\bar{c}_s$ = average surface concentration of hydrogen, g. moles/cc.
d = particle diameter, cm.
D = bulk diffusion coefficient in liquid, sq.cm./sec.
D_{eff} = effective diffusion coefficient in porous catalyst, $= D\theta/\tau$, sq.cm./sec.
E_D = activation energy for bulk diffusion, cal./g.mole
E = activation energy for intrinsic kinetics of reaction, cal./g.mole
g = acceleration due to gravity, cm./sq.sec.
h_T = total holdup, g.
h_S = static holdup, g.
h_D = dynamic holdup, g.
k_L = liquid phase absorption mass transfer coefficient, cm./sec.
k_{Ls} = mass transfer coefficient through liquid film, cm./sec.
k_s = dissolution mass transfer coefficient, cm./sec.
k_v = intrinsic rate of reaction constant per unit volume of catalyst pellet, for first-order reaction, cc. fluid/(cc. cat. pellet) (sec.)
L = liquid flow rate, cc./sec.
N = number of particles
N_{Re} = Reynolds number, $L\rho\pi/d\mu$
dn/dt = observed rate of reaction, g.moles/sec.
r = distance from center of pellet, cm.
R = radius of particle, cm.
t = time, sec.
U = local velocity, cm./sec.
U_i = velocity of liquid film at outer surface, cm./sec.
V_c = volume of catalyst particles in reactor, cc.
x = distance in a radial direction from outer liquid surface, cm.

Greek Letters

γ = coefficient of surface tension, dynes/cm.
Γ = mass flow rate of liquid per unit cross section of bed, g./(sec.) (sq.cm.)
Δ = liquid film thickness, cm.
$\bar{\Delta}$ = average liquid film thickness, cm.
ϵ = fraction of reactor volume not occupied by catalyst particles (in absence of liquid)
η = effectiveness factor
θ = angle, Equations (1) to (5)
θ = void fraction of catalyst, cc./cc.
μ = viscosity, g./(sec.) (cm.)
ρ = density, g./cc.
τ = tortuosity factor, empirical factor to correct for tortuosity and for non-uniformity of pore cross section, $\tau = D\theta/D_{\text{eff}}$
ϕ_s = Thiele modulus for a first-order reaction, $R\sqrt{k_v/D_{\text{eff}}}$

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